PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Apparatus for the Direct Analysis of Spectral Lines

We, REGIE NATIONALE DES USINES RENAULT, a French Body Corporate, of 8/10, Avenue Emile Zola, Billancourt (Seine) France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The use of spectrum technique for analytical purposes is taking an increasingly important place in industrial laboratories and research laboratories, by reason of its rapidity, its sensitivity and its accuracy.

This technique consists in analysing the spectrum of the light emitted by a spark or an arc struck, for example, between two electrodes, of which one is constituted by the material to be analysed.

In the present specification, certain expressions and terms of art are employed corresponding to those in current use in the technique concerned. These expressions and their definitions for the purposes of the present specification are as follows:—

By the term "evolution" and its derivatives is meant the course of the value of a parameter with respect to time irrespective of whether the parameter is varying or constant.

By "striking period" is meant the initial building-up period of the spark before the electrical currents and other parameters have reached a sufficiently stable condition for measurement.

The "sparking period" is the period of time for which the sample is subjected to electrical excitation, in the form of sparking or arcing.

The "integration period" is the sparking period less "the striking period".

Although they are more rapid than chemical processes, the usual spectrum methods employing a photographic emulsion as a receiver have proved in their turn to be too slow. The recent appearance of the so-called "direct-reading" spectral techniques using photo-electric cells as receivers, has the advantage of increased rapidity and greater accuracy. These techniques have been especially developed up to the present time in connection with analysis by emission. For example, they permit of analysis of the metal during the course of its preparation in foundries and steel-works. In addition, these "direct-reading" techniques have proved superior to the standard techniques in connection with investigation of spectral processes and they provide an easier development of analytical methods of operation.

Apparatus known at the present time for direct spectral emission analysis use photo-electric cells as receivers and generally give the measurement of the ratios of the intensities of the analysis lines to the intensities of the reference lines (internal standard method). Such apparatus is divided into two classes:

1.—Certain apparatus of the so-called exploring cell type comprise two photo-electric cells, one being in position on a reference line and the other moved by an automatic mechanical device, exploring the spectrum by taking successively different stopping positions on the lines to be analysed. During the passage of the spark, a recorder gives the measurement of the intensities of the successively-explored lines, these intensities being referred to that of the reference line.

The known apparatus of this type give an "evolutionary" measurement, that is to say the ratio of intensities ("reference and exploration"), is recorded as a function of time.

These apparatus have the following advantages:

a) They employ only two photo-electric cells,

b) They enable any line whatever of the spectrum to be studied,

c) They permit any spectral line to be put in the analysis programme at very little cost,

d) They enable the evolution of the ratio of intensities of one pair of lines to be studied during the sparking period,

e) The electrical part of the apparatus is relatively simple.

On the other hand, however, these apparatus have the following drawbacks:

a) It is necessary to use the same reference line for all the analysis lines,

b) The reference line must be taken outside the band covered by the analysis lines. For this reason, the ratios of intensities for the analysis lines furthest removed from the reference line vary with time due to variations in transparency of the optical system, as a result of dust, condensation of vapour, etc.,

c) The changing of the reference line is a delicate manual operation,

d) Since the lines are explored successively in order of wave-length, the "striking periods" increase for the lines taken in that order, and are not always favourable to accuracy of the analysis Thus, these apparatus permit of the study of the evolution of the ratios of the lines as a function of time, and enable the most favourable periods of "striking" to be deduced therefrom, but they hardly allow the conclusions of these studies to be put into practice in analysis programmes,

e) Since the lines are explored individually and successively, the total duration of the analysis (although less than with the photographic method) may be considered excessive,

f) These apparatus do permit the study of the evolution of the ratio of intensity of one pair of lines during the sparking period, but not the variation in intensity of one single line during the sparking period.

2.—Other so-called multiple-cell apparatus comprise a greater number of photo-electric cells; some of these are in position on the analysis lines, and the others are in position on reference lines. During the sparking, and after a certain striking period, the currents delivered by the photo-electric cells charge condensers. The sparking ceases at a pre-determined voltage across the condenser of the reference line, and then the voltages across the condensers of analysis lines are measured. A number of analysis programmes are available, of which each one is characterised by the choice of the reference line and by the selection of the analysis lines.

The known apparatus of this kind are of the integrating measurement type, that is to say they give integrals of intensities during the time necessary to reach the pre-determined voltage on the condenser of the reference line.

These apparatus have the following advantages:

a) The reference lines can be taken from any region whatever of the spectrum,

b) The change of analysis programme is instantaneous, and is carried out by a simple switching operation,

c) Since the lines are analysed simultaneously, the total duration of analysis is reduced.

On the other hand, however, these apparatus have the following drawbacks:

a) In each analysis programme, the same line serves as a reference for all the analysis lines,

b) All the condensers begin to charge at the same time, and the period allowed for "striking" is the same for all the lines,

c) All the condensers complete their charging at the same time, and the integration period is the same for all the lines,

d) These apparatus do permit the study of the evolution of intensity of one line during the sparking period, but not the evolution of the ratio of intensities of a pair of lines during the sparking period,

e) The composition of the analysis programme is strictly fixed in a definite manner, and cannot be altered at will,

f) The design of the automatic systems is complicated.

The direct-analysis apparatus which forms the object of the present invention is related to those of the second type: it comprises a certain number of photo-electric cells, one cell per line. For this reason, it has the above-detailed advantages inherent in this class of apparatus, but as compared with all the apparatus produced up to the present time it possesses in addition the following advantages:

a) In an analysis programme, different reference lines can be associated with the different analysis lines,

b) Different "striking" periods and different integration periods can be used for the different lines,

c) The measurements are carried out during the course of the sparking period, which results in the shortest possible period of analysis,

d) The analysis programmes are prepared according to requirements. Thus, it is easy to introduce into a programme a fresh pair of lines (chosen from the lines provided with photo-electric cells); it is easy to change the analysis programme, for example so as to change to the analysis of a different material,

e) The design of the automatic systems and the electronic apparatus is relatively very simple.

f) The greater part of the apparatus is made up of interchangeable assemblies, which results in easy rectification of faults,

g) In addition to its main function of current analysis by integration, the apparatus permits the easy study, for the purposes of research or preparation of programmes of current analysis, of the evolution of the intensity of any line during the sparking period, together with the evolution of the ratio of intensities of any pair of lines during the sparking period,

h) In addition to its main function of current analysis by integration, the apparatus permits the easy measurement, for the purposes of control of operation of certain members, of the dark currents of photo-electric cells, together with the photo-electric currents delivered under an auxiliary illumination, and of the ratio of these photo-electric currents taken in pairs,

i) The choice of the function of the apparatus is very simply made by the single operation of a change-over switch.

The device known as a spectro-receiver which forms the object of the present invention is capable of use in co-operation with any system whatever which can generate a spectrum.

The system producing the spectrum does not form any part of the invention. Very generally, it comprises:

1) a source, excited by a suitable device so as to emit radiation;
2) the material to be examined, subjected to this primary radiation in order to produce a secondary radiation;
3) a suitable system which analyses the secondary radiation and produces a spectrum.

In certain cases, all the above-mentioned elements are present, for example:

a) Systems producing a spectrum of fluorescence (for example X-ray fluorescence),

b) Micro-analysers using electronic probes,

c) Systems producing an absorption spectrum (for example ultra-violet, visible, infrared).

In other cases, some of the elements are not present, for example:

a) Systems producing a diffraction spectrum (electronic or X-ray). The material to be examined, subjected to a radiation (electronic or X-ray) and decomposing this radiation into a diffraction spectrum, itself plays the part of the analyser system referred to under 3.

b) Systems producing an emission spectrum. The material to be examined, excited by a suitable device, produces a radiation and in this case the material itself carries out the function of the source referred to under 1.

The spectro-receiver which forms the object of the present invention is capable of use with any system which produces a spectrum, but has a particular advantage in all cases in which the intensity of the spectral lines varies as a function of time. The most important of these cases is that of emission spectrum analysis, in which the phenomena that are promoted by sparking have a marked evolutionary character, resulting in fluctuations and variations of the intensities of the spectral lines and of the ratios of their intensities. It is for this reason that the spectro-receiver will be described in the text below, in certain aspects, for the particular case of the reception of an emission spectrum.

Thus it will be assumed (and this is actually obtained in known manner in certain emission analysis apparatus) that the system producing the spectrum comprises a source of radiation which produces, outside the sparking periods, an illumination taking the place of the spectrum so as to render the photo-electric cells more stable. This device will be termed a "non-spectral irradiation device". This auxiliary non-spectral irradiation may also serve as the reference irradiation.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made to the accompanying drawings, in which:—

Fig. 1 is a diagram of a unit hereinafter referred to as a "working unit";

Fig. 2 is a diagram of an integration unit;

Fig. 3 is a diagram of the control centre;

Fig. 4 is a diagram showing the inter-connection of the various elements;

Fig. 5 is a diagrammatic view showing the arrangement of the parts on a panel.

The spectro-receiver comprises essentially (see Fig. 4):

a) An assembly of intensity sources of which two are shown 66,

b) An assembly of working units of which two are shown 67,

c) An assembly of integration units of which two are shown 68,

d) A control centre 69,

e) Two electronic amplifiers 72 and 73,

f) An electronic recorder 74.

The spectro-receiver has essentially two distinct functions: one a so-called "Evolution" function for recording as a function of time the ratio of two photo-electric currents (instantaneous value), and serving for the purposes of research and adjustment; the other a so-called "integration" function for the measurement of the ratio of two photo-electric currents integrated during a period of time and used for the analysis of elements.

I—*Intensity sources 66*

The spectro-receiver receives different radiation fluxes:

1) Fluxes derived respectively from the different lines selected in the spectrum. In the following description, these fluxes will be referred to as "spectral fluxes".

2) When so required, a light flux taken before the spectral decomposition of the radiation; in the description which follows, this flux will be referred to as the "whole flux".

3) When so required, in substitution of the fluxes defined under the paragraphs 1 and 2) above, fluxes derived from the non-spectral irradiation device; in the following description, these fluxes will be termed "non-spectral fluxes"; they enable the cells to be illuminated during the times of rest in order to make them more stable, and serve in addition to verify the reproduction of the response of the apparatus.

The spectro-receiver comprises a certain number of sources of current which will hereinafter be referred to as in the description. "Intensity sources". These sources comprise:

1) Devices of known type which convert the light fluxes (the whole flux and the spectral fluxes or alternatively the non-spectral fluxes into electrical currents). These devices which are known in the following description as "photo-electric receivers" or photo-electric cells, may be for example electronic photo-multiplying cells. They may comprise in known manner individual sensitivity adjustments.

2) In accordance with a particular arrangement of the invention, a device generating an electric current which is constant with respect to time. This device will be termed in the following description a "Source of Constant Intensity". In the case in which the photo-electric cells are electronic photo-multiplying cells, the source of constant intensity can be produced by causing the high-tension supply of these cells to deliver into a resistance of high value.

II—*Working units 67*

These interchangeable units are associated one with each of the intensity sources. An example of embodiment of a working units is shown diagrammatically in Fig. 1. These units play a different part, depending on the function selected at the control centre.

1) In the integration function and during the sparking period, a continuous supply voltage is obtained from the terminal 1; the relay 2 is energised; the condenser 3 (10 micro-farads) is charged by being connected to the terminal 4 which receives the output from the associated intensity source; the charging voltage appears on the terminal 5.

2) For the evolution function and also outside the sparking periods, the relay 2 is de-energised and the condenser 3 is short-circuited to earth through a resistance 6 (1,000 ohms). When the relay 2 is de-energised the intensity source delivers into the impedance constituted by the resistance 14 (1 megohm) and the capacitor 15 (0.5 micro-farad) in parallel. If the switch 7 is in the position 8, or "zero" position, the associated intensity source 66 delivers to earth; if the switch 7 is in the position 9, known as the "T" position or in position 10, known as the "X" position, the voltage at the terminals of this impedance appears on the terminal 12 or on the terminal 13 respectively; in addition, the indicator lamp 11 is lighted.

III—*Integration units 68*

These interchangeable units are each associated with one pair of working units. An example of an integration unit is shown diagrammatically in Fig. 2.

The terminals 16 and 17 of the integration unit are connected to the terminals 5 of two working units and for the integration function they receive, during the excitation, the charging voltages obtained from these two units; under certain conditions namely when the relay 34 is energised, these voltages are transmitted to the terminals 18 and 19.

The integration unit, the automatic features of which are actuated by the motor 20, only operates when the switch 21 is closed, which is indicated by the signal lamp 22, and when an alternating supply voltage is applied to the terminal 23, which takes place during the sparking period when working on integration.

Under these conditions, the motor 20 starts up at the same time as the sparking. It drives a self-contained system of chrono-relays which produce consecutive time intervals (O-T1) duration of "striking"; (T1-T2) duration of integration and (T2-T3) duration of measurement. The striking and integration periods are programmed and can be varied at will. The duration of measurement is not programmed and is fixed once and for all (at a value for example of two seconds).

The self-contained time-relay device comprises electric contacts 24, 25 and 26. The instant of starting of the spark being taken as the origin of time, the contact 24 which is open at instant 0, closes at the instant T1; the contact 25, open at instant 0, closes at the instant T2 and opens at the instant T3; the contact 26, closed at instant 0, opens at the instant T3. The return of the contacts 24 and 26 to their initial positions at the end of the sparking period is effected by a device 27 connected to the terminal 28, to which is applied a continuous voltage of 24 volts during the sparking period.

During the striking period (from 0 to T1) the relay 29 remains de-energised; the points 30 and 31 are connected to earth; the condensers 32 and 33 of low value (1,000 pico-farads) with respect to the condensers 3, remain connected in parallel with the condensers 3 of the associated two working units.

At the instant T1, the contact 24 closes and the relay 29 is energised whereby the points 30 and 31 are disconnected from earth. During the integration period (from T1 to T2), the capacities 32 and 33 retain the charges acquired at the instant T1, playing the part of a memory, and the voltages at the points 30 and 31 represent the increases in the charging voltage of the associated condenser 3, starting from the instant T1.

During the measurement period (from T2 to T3) the transient closure of the contact 25 controls the working of the relay 34. During this period, the increases in charging voltage corresponding to the integration period are transmitted to the terminals 18 and 19, and on the other hand a continuous voltage appears on the terminal 35. This period is indicated by the lighting of the signal lamp 36.

At the instant T3, the contact 26 opens, the motor 20 stops, and the alternating voltage at the terminal 37 disappears.

IV—*Control centre—Amplifiers and recorder*

An example of embodiment is shown diagrammatically in Fig. 3.

By means of a change-over switch with four positions, the control centre enables the function of the spectro-receiver to be selected.

1) *Integration function*

The apparatus permits of the measurement of the spectral fluxes of a number of lines during the course of a single sparking period.

The measurement of each spectral flux is effected at will either as an absolute value (that is to say with respect to the source of constant intensity) or as a relative value. In the second case, it can be related at will either to the spectral flux of a reference line, or to the whole flux.

The measurement of the spectral flux of each line is effected during the course of the sparking period as an average value (measurement of the absolute value) or as a ratio of average values (measurement of relative values) with respect to a period, known as the integration period, the limits of which are selected at will for the line considered.

This function is used for the current practice of analyses. It always consists of the measurement of the ratio of the integrated outputs of two intensity sources, this measurement being carried out for several pairs of intensity sources during the course of a single sparking period.

The position 39 of the switch 38 corresponds to the integration function.

The relay 43, supplied with a continuous current from a source 43*a* is energised. Outside the sparking periods, the sparking source does not transmit any voltage to the terminals 44 and 45. The relay 46 is de-energised. The non-spectral irradiation device 71, connected to the terminal 47, is supplied with an alternating voltage; the photo-electric cells are subjected to the non-spectral irradiation flux.

At the instant 0 of initiation of the sparking, an alternating voltage derived from the sparking source appears at the terminals 44 and 45. The relay 46 is energised. An alternating potential is transmitted over the connection 48 and as the relay 43 is energised, this voltage is transmitted, on the one hand to the terminal 49, connected to the terminals 23 of each of the integration units, which has the effect of putting into operation all the integration units included in the programme, that is to say, of which the switch 21 is closed, and on the other hand to the coil of the relay 52.

If no integration unit is recorded on the programme, that is if all the switches 21 are open, no voltage appears on the terminal 50 connected to the terminals 37 of all the integration units, and the relay 51 remains de-energised. At the instant of initiation of the spark, the relay 52 is energised. This relay being retarded (by a fraction of a second) the short circuit of the terminals 53 and 54 is opened shortly after the initiation of the spark. The terminals 53 and 54 are connected to a special circuit from the sparking source, so that the sparking is only possible when this circuit is closed. In consequence, if there is no integration unit entered on the programme, the sparking only lasts for a fraction of a second.

If a number of integration units are entered on the programme, an alternating voltage derived from the terminals 37 of these units appears on the terminal 50, and the relay 51 is energised as soon as the spark has been started. In consequence, the energising of the relay 52, occurring a fraction of a second after the starting of the spark, does not result in the breaking of the spark.

In this case, each integration unit operates under its own automatic control, and the alternating voltage at the terminal 37 disappears at the instant T3.

On the terminal 50, the alternating voltage disappears at the instant T3 maximum (the highest value of all the periods T3 corresponding to all the integration units entered on the programme). In consequence, the sparking is interrupted as soon as all the integration units entered on the programme have completed their cycle, including the period of measurement.

At the instant at which the sparking ceases, the alternating voltage derived from the sparking source and applied to the terminals 44 and 45 is interrupted. The relay 46 goes back to its position of rest, which has the result of interrupting the alternating

voltage of 115 volts at the terminal 49, and returning all the integration units to the position of rest.

During the sparking period, the relay 46 is energised, causing a continuous voltage to be transmitted to the terminal 55; this voltage supplies the working units 67 (terminals 1) and the integration unit 68 (terminals 28).

The terminal 56 is connected to the terminals 35 of all the integration units. It receives a continuous voltage during the measurement periods corresponding to the various integration units entered on the programme. During each of these periods, the relay 57 is energised.

The terminals 58 and 59 are respectively connected to the terminals 18 and 19 of all the integration units. During the course of each period of measurement, they thus receive the signals coming from an integration unit and thus from two intensity sources.

The terminals 60 and 61 are respectively connected to the inputs of two amplifiers of known type which act as impedance changers Outside the measurement periods, the inputs of the two amplifiers are connected to earth; during the measurement periods they receive the signals.

A recording potentiometer of known type receives the output voltages of the two amplifiers and gives a measurement of their ratio. The paper-winding motor of this recorder is supplied from the terminal 62 which, by reason of the operation of the relay 57, is only supplied with alternating voltage during the measurement periods. In consequence, the paper is only unwound during the periods of measurement.

2) *Evolution/spectral irradiation function*

The evolution or variation of the spectral flux of one line or of the ratio of the spectral fluxes of two lines, or of the ratio of the spectral flux of one line to the whole flux is studied during the course of the sparking period. This function is useful in fixing the operating conditions of the integration programme by the rational search for the best conditions of sparking and of time-delay of the integration.

The position 40 of the switch 38 corresponds to the "evolution-spectral irradiation" function.

The relay 43 is de-energised.

The control of the non-spectral irradiation device connected at 47 is effected, as for the integration function, by the action of the relay 46; the device is only supplied outside the sparking periods.

By the action of the same relay, the relay 57 is supplied with a continuous voltage during the entire sparking period. The measurement period (unwinding of the paper of the recorder and transmission of the signals to the amplifiers) is thus identified with the sparking period. The signals, derived from the terminals 63 and 64 which are respectively connected to the terminals 12 and 13 of all the working units 67, are proportional to the outputs of the two intensity sources selected by the evolution programme.

The interruption of the sparking is not determined by the action of the relays 51 and 52, which remain at rest, but by the manual opening of the circuit of the terminals 53 and 54 by means of a push-button 65.

3) *Evolution — Non-spectral irradiation function, and Evolution—Non-irradiation function*

These two functions permit of the control of the response of the photo-electric cells which are subjected either to the non-spectral constant fluxes of light or are placed in darkness. They are only distinguished from each other by the putting into or out of service of the non-spectral irradiation device.

These two functions are respectively determined by the positions 41 and 42 of the change-over switch 38. In both cases, the relay 43 is de-energised and the relay 57 is energised.

The measurement is thus continuous and the signals derived from the terminals 63 and 64, respectively connected to the terminals 12 and 13 of all the working units are proportional to the outputs of the two intensity sources selected in the evolution programme.

Fig. 4 indicates the wiring diagram of the various parts of the circuits. There are again indicated in diagrammatic manner:

— The intensity sources 66 (two intensity sources are shown),
— The working units 67 (two working units are shown),
— The integration units 68 (two integration units are shown),
— The control centre 69,
— The sparking source 70,
— The non-spectral irradiation device 71,
— The amplifier 72 of channel T,
— The amplifier 73 of channel X,
— The recorder 74,
— The outputs 75 of the intensity sources,
— The outputs 76 and 77 of a voltage the duration of which is identical with the sparking period,
— The outputs 78 and 79 of a circuit, the closure of which makes the sparking possible,
The supply of the non-spectral irradiation device 80,
— The signal input of the amplifier T at 81,
— The signal output of the amplifier T at 82,
— The signal input of the amplifier X at 83,
— The signal output of the amplifier X at 84,
— The inputs 75 and 86 of the two signals to the recorder,
— The supply 87 of the paper-unwinding motor of the recorder.

Fig. 5, shows a practical form of work-

ing of the apparatus. It will be seen that the working units 67 are arranged in a row and are coupled by removable connections to the integration units 68 arranged in two further rows, one on each side of the first. This judicious arrangement enables for example the couplings intended for analyses of elements, which remain permanently on the apparatus, to be grouped on one side, while the couplings intended for occasional research, and which can be modified at will, are arranged on the other side.

In a last row are arranged the amplifiers 72 and 73, the control centre 69 and the supply 80.

It should be observed that in the above description, the supply voltages which have been referred to as "continuous voltages" may be for example 24 volts, and those referred to as "alternating voltages" may be 115 or 230 volts 50 cycles. The numerical indications of voltage, resistance, capacity and time, and the indications of the nature of the current (alternating or continuous), have only been given by way of example in an embodiment.

The operation and the advantages of the apparatus are made clear by the following observations:

The programme of an evolution function consists in the choice of the two intensity sources which are to be employed. This programme is entered by the action of the switches 7 of the working units. It is continuously indicated by the signal lamps 11 of these units.

The possibility of registering a programme and the indication of the programme registered are continuous; they exist even during the use of the spectro-receiver in the integration function. It is thus possible to prepare an evolution programme during integration operations.

In order to enter or register an evolution programme, the change-over switch 7 associated with the intensity source to be studied is placed in the position "X", and the change-over switch 7 associated with the intensity source taken as a reference is placed in the position "T"; all the other switches 7 are in the "zero" position. Only the signal lamps 11 corresponding to the two intensity sources selected are then lighted.

In the function evolution—non-irradiation, the source of constant intensity will almost be taken as the reference, and the dark current of a photo-electric cell will be recorded.

In the Evolution—non-spectral irradiation function, the ratio will be recorded of the outputs of two photo-electric cells illuminated by the non-spectral irradiation device; or alternatively, taking as a reference the source of constant intensity, the output will be recorded of a single photo-electric cell, illuminated by the non-spectral irradiation device. In this way, the fidelity of the photo-electric cells can be checked from the point of view of sensitivity.

With the evolution—spectral irradiation function, the source of constant intensity can be taken as a reference, and the variation of the spectral flux of one line will be recorded. This process will be used for certain researches and for the determination of the conditions of timing to be adopted for the measurement of the absolute value of the spectral flux of the line considered with the integration function. It will also be currently used for the adjustment of the position of the outlet slits with a view to compensating for the displacements of the spectrum, this adjustment being usually known as "profiling". It is also possible, again in the evolution—spectral irradiation function, to record the evolution of the ratio of the spectral fluxes of two lines, or of the ratio of the spectral flux of one line to the whole flux. This process will be used for certain research and for the determination of the conditions of timing to be adopted for the relative measurement of the spectral flux of one line in the integration function.

In the case where the outlet slits are mounted on several blocks which have to be independently adjusted in position, this last process may also be used for "profiling" by obtaining the ratio of the intensity of one line of a block which is displaced, to the intensity of a line of a block which is held fixed, this method of operation having the advantage of reducing the fluctuations on the recording.

The programme for the integration function consists in the choice of the pairs of intensity sources to be examined during the course of a sparking period. This programme is registered by the action of the switches 21 of the integration units. It is continuously indicated by the signal lamps 22 of these units.

The timing of a programme of integration consists in the adjustment of the periods of striking and integration in the integration units registered on the programme. The only condition to be observed is that the periods of measurement do not overlap.

The possibility of registering and timing the programme and the indication of this programme are continuous; they exist even during the use of the spectro-receiver in the evolution function. It is therefore possible to prepare an integration programme during evolution operations.

In order to work in the integration function, it is unnecessary to wipe out the evolution programme, and conversely, when working in the evolution function it is unnecessary to wipe out the integration programme. In order to transfer from one function to the other, it is only necessary to operate the single change-over switch 38 of the control

centre.

In the Evolution function, it is permissible to carry out all the couplings possible in the unit of the intensity sources. In a unit of N intensity sources, there may be 1/2 N (N—1) distinct couplings. All these couplings can be effected by a simple registration in the evolution programme.

In the integration function, a single working unit can be connected to a number of integration units, and thus all possible couplings can also be effected. When a current source is associated with a number of couplings, its output is the subject of a number of integration measurements carried out with different time intervals; the time intervals associated with the various couplings are thus chosen independently with the single reservation that the short periods of measurement do not overlap.

To sum up, all possible couplings can be carried out and their timing periods may be chosen independently. All the couplings provided, that is to say corresponding to installed integration units, can be carried out by simple registration in the integration programme. Exceptional couplings are possible by the simple suitable connection of the inputs 16 and 17 of supplementary integration units.

In the use of the integration function, the measurement of the spectral flux of each line may be made by proper value, or referred to the whole flux, or referred to the spectral flux of a reference line. In the latter case, the lines examined in a single programme of integration may be compared to different reference lines. These three methods of measurement may be co-existent in the same programme of integration.

When the measurements are effected relative to a reference line (the so-called "internal standard" method) it is just as easy to change the selection of a reference line as to change the selection of a line to be examined; it is only necessary to delete from the programme one integration unit, and to register in the programme another unit in its place.

The spectro-receiver thus lends itself perfectly to the examination in the same apparatus of various substances which differ in the basic element; for example to the spectral analysis by emission of ferrous allows, light alloys, etc. on the same apparatus.

The adjustment of the timing of the integration units is not of a critical nature. A difference in the value fixed for T1 or T2, such as may be produced from one adjustment or the next, does not alter the results, since the quotient is measured of the integrals of two varying magnitudes, these integrals being both taken between the same limits of time.

The measurements are not carried out subsequently to the sparking period but during the actual course of that period. The sparking continues for precisely the time necessary in order that all the measurements required by the programme may be made.

The operation of the spectro-receiver is not restricted to a limited number of rigidly fixed programmes, but is on the contrary very flexible, giving extensive possibilities within the framework of an extension of the number of working and integration units.

It is to be understood that the foregoing description of a particular form of embodiment has been given especially by way of example, and that it would be possible to make numerous modifications and alternative forms of the elements forming part of the apparatus described, without thereby departing from the scope of the invention.

WHAT WE CLAIM IS:—

1. In a spectro-chemical analysis system having a sparking source for exciting emission of light from a sample, and a light-dispersing system, an apparatus for simultaneous evaluation of a plurality of chemical elements during the same sparking period, said apparatus permitting measurement at will of the instantaneous and integrated values of currents generated during said sparking period and comprising means for delivering a constant current, means for receiving said light from said sample and for generating output currents proportional to the intensity of light received, said means for receiving said light including a plurality of photo-electric cells, said cells being each excited by a radiation of definite different wavelength, means for integrating selectively said outputs currents over selected periods of time, recording means for recording the ratio of said constant current to said output currents in instantaneous value measurement and also for giving a recorded integration of said outputs currents immediately at the end of said time periods in integrated value measurement, and programme control means for preselecting and varying the operating cycle of said apparatus, and for varying said periods of integration.

2. In a spectro-chemical analysis system having a sparking source for exciting emission of light from a sample and a light-dispersing system, an apparatus for direct analysis of emission spectra, said apparatus permitting measurement at will of instantaneous or integrated values of currents generated during the sparking period and comprising a plurality of sources of current, of which one is a source of constant current, the other said sources being each constituted by a photo-electric cell adapted to be excited by light of definite wavelength; a plurality of working units associated one with each current source, each working unit comprising an integration condenser which, in integration measurement, is charged by the as-

sociated current source during the sparking period, an impedance which, in instantaneous measurement, receives the current from said associated source, relay means for connecting the current from said associated source either to said condenser or to said impedance, and a switch for short-circuiting said impedance; a plurality of integration units each associated with a pair of said working units and intended to receive a charging-voltage from the integration condenser of each said pair of working units, said integration units each comprising an independent time-relay system, charge transmission condensers each arranged to be connected in parallel with one of the integration condensers, relay means for transmitting the increases in charging voltage received by said charge transmission condensers during an integration period, and switches for putting said integration units into or out of circuit; a control centre permitting the measurement of the ratio of the current generated by each of said other current sources to the current from said source of constant current, or alternatively to a reference flux or to a total flux of undispersed light, said control centre comprising first and second terminals, first relay means for applying, upon initiation of sparking for integration measurement, an alternating voltage to said first terminal, which first terminal is coupled to all said integration units, the second terminal being arranged to receive an alternating voltage when said first relay means has applied alternating voltage to said first terminal provided that at least one of said integration units has been put into circuit by means of said switch thereof, said second terminal supplying second relay means of the control centre for actuating a switch disposed in a sparking circuit, said second relay means causing sparking to be cut-off as soon as all said integration units in circuit have completed their cycle, the first relay means further applying a direct-current potential to said working units to cause the integration condensers to be placed in circuit and to said integration units to initiate operation of the same, said control centre being further coupled to amplifier means and to recording means giving the ratio of output voltages of said amplifier means, third and fourth terminals of said control centre being coupled to all said working units in such manner that said third and fourth terminals receive signals from one working unit or a pair of working units for an instantaneous measurement, further terminals of said control centre being coupled to said integration units for receiving the increases in voltage received by said charge transmission condensers, and a switch for selecting instantaneous or integration measurement.

3. Apparatus as claimed in Claim 1 or 2, wherein the source of constant current is formed by supplying a stabilized voltage to a stable resistance of high value, said resistance supplying a reference for measuring the real values of the integrated intensities of said generated currents, and also a reference for recording the values of the instantaneous intensities of said generated currents.

4. Apparatus as claimed in Claim 1, wherein said cells and the source of constant current are each associated with a working unit, each working unit including relay means which, depending on whether an integration or instantaneous function is to be determined, causes the current from said associated source to be directed to an integration condenser of the unit or to an impedance of the unit.

5. Apparatus as claimed in Claim 2 or 4, wherein the integration condenser of each working unit is short-circuited by a low value resistance during such times as said current from the associated source is directed to said impedance.

6. Apparatus as claimed in Claim 2, 4 or 5, wherein each said working unit comprises a three-position switch by means of which the current from said associated source is, in the instantaneous measurement position of the relay means of the working unit, short-circuited to earth or is directed to one or the other of signal output terminals of the working unit, operation of said three-position switch serving to enter the associated unit in or remove the same from a programme of instantaneous measurement.

7. Apparatus as claimed in Claim 6, wherein signal output terminals of all said working units are selectively connected to two common lines in order that the signal ratios may be measured and recorded.

8. Apparatus as claimed in Claim 4, wherein said means for integrating include a plurality of integration units each of which is coupled to two working units, each integration unit having charge transmission condensers arranged to be connected in parallel with one of the integration condensers, relay means for transmitting the increases in charging voltage received by said charge transmission condensers during an integration period, and switches for putting said integration units into or out of circuit.

9. Apparatus as claimed in Claim 2 or 8, wherein said integration units are coupled to said working units by removable electric couplings, thereby enabling any two of said current sources to be selected for measurement of the ratio of their intensities, said intensities being then integrated during the same period of time.

10. Apparatus as claimed in Claim 8, and further including a control centre permitting the measurement of the current generated by each of said associated current sources

relative to the current from said constant current source or relative to the current generated by a reference flux or a total flux of undispersed light.

11. Apparatus as claimed in Claim 10, wherein each said integration unit comprises a motor-driven independent time relay system.

12. Apparatus as claimed in Claim 2 or 11, wherein the cycle of the time-relay system is started by a signal from the control centre of said apparatus and said system includes three electric contacts, one of said contacts closing at the end of the striking period to permit the operation of a contact breaking relay which disconnects charge transmission condensers from earth, the second of said contacts closing at the beginning of the measurement period, and opening at the end of said period, said second contact enabling a further relay to be energised so as to transmit the variations in charge of said integration condensers through said transmission condensers, and the third contact opening at the end of the measurement period to stop a motor driving said time relay and to remove the voltage on a terminal connected to said control centre whereby sparking is stopped.

13. Apparatus as claimed in Claim 12, wherein each said integration unit comprises two charge transmission condensers connected to the integration condensers of the associated working units, whereby the voltages acquired by said integration condensers during the striking period may be stored in order to measure the increase in charge of said integration condensers during the integration period only.

14. Apparatus as claimed in Claim 13, wherein one plate of each said two charge transmission condensers is constantly connected to the non-earthed plate of the associated integration condenser, the other plate of each said charge transmission condenser being isolated from earth by said contact breaking relay at the moment of initiation of the integration period.

15. Apparatus as claimed in Claim 11, 12, 13 or 14, wherein the further relay, upon energisation thereof, transmits a control voltage which actuates a paper-unwinding device of said recording means.

16. Apparatus as claimed in Claim 15, wherein the charge transmission condensers of the integration units are selectively connected to two common lines which are connected to said recording means.

17. Apparatus as claimed in any one of Claims 11 to 16, wherein each integration unit comprises a manually operated switch which, when closed, enables the associated time relay system to be supplied whereby the integration unit is entered in a programme of integration measurement.

18. Apparatus as claimed in Claim 10, wherein said control centre includes first relay means operated upon initiation of sparking thereby to apply an alternating voltage to a first input terminal of each integrating unit thereby to commence operation of the time relay system of each of said integration units which is entered in an integration programme said first relay further serving to apply a direct current to the relay means of said working units.

19. Apparatus as claimed in Claim 18, wherein amplifier means are connected between the control centre and the recording means for amplifying the signals applied to the recording means.

20. Apparatus as claimed in Claim 2 or 19, wherein said control centre includes a four-position switch, said switch permitting selection of any one of the functions:—

— "Integration": measurement of the integrated intensity ratios of different pairs of sources of current in a spectral irradiation operation of the photo-electric receivers.
— "Evolution—spectral radiation": measurement of the ratio of momentary intensities of a pair of sources of current in a spectral irradiation operation of the photo-electric receivers.
— "Evolution — non-spectral radiation": measurement of the ratio of the momentary intensities of a pair of sources of current in a non-spectral irradiation operation of the photo-electric receivers.
— "Evolution — non-radiation": measurement of the ratio of momentary intensities of a pair of current sources in a non-irradiation operation of the photo-electric receivers.

21. Apparatus as claimed in Claim 20, wherein the control centre includes third relay means which is operated upon said four-position switch of the control centre being set to record an integration function, supply of said alternating voltage to said first input terminal of the integrating and supply of direct current to the relay of each working unit being possible only upon operation of said second relay means.

22. Apparatus as claimed in Claim 2 or 19, wherein said amplifier means consist of impedance matching amplifiers and said recording means include a potentiometer giving the ratio of the output of said amplifiers.

23. Apparatus as claimed in Claim 22, wherein the contacts of said third relay means cause the integrated value signal from the integrating units or the instantaneous value signal from the working units to be directed to the amplifiers.

24. Apparatus as claimed in any preceding claim, wherein the said sparking source includes a sparking circuit provided with a safety push button which enables sparking

to be cut off at any time.

25. Apparatus for direct analysis of emission spectra, the apparatus being substantially as hereinbefore described with reference to the accompanying drawings.

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Fig.1

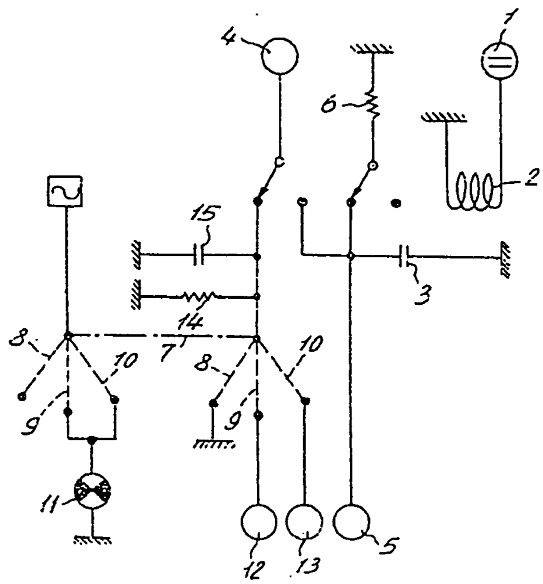
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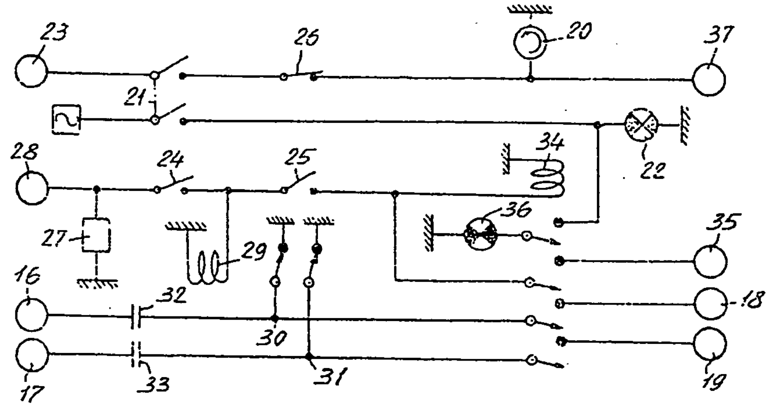
Fig.2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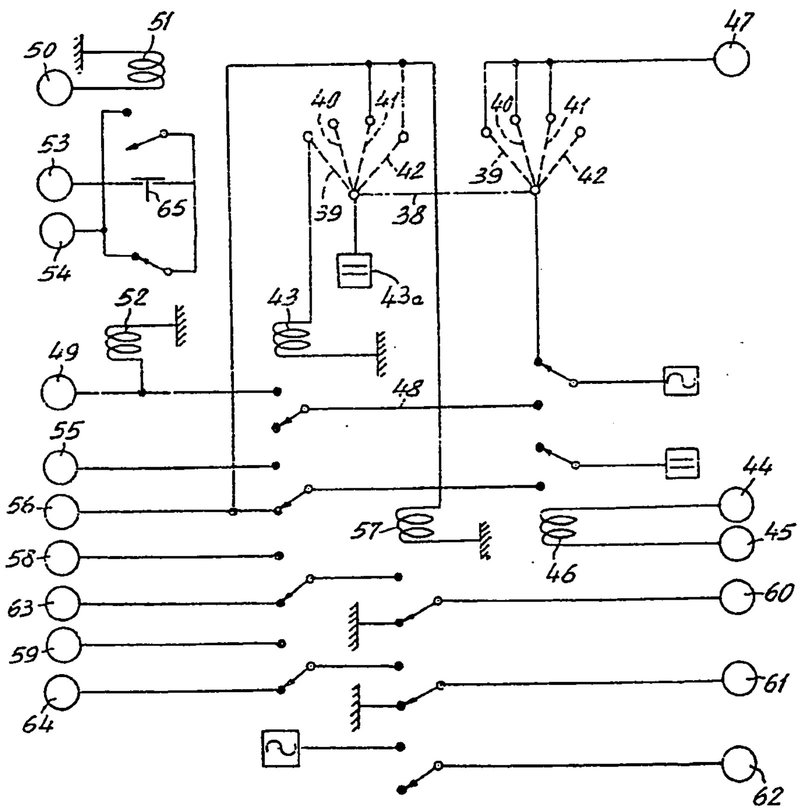
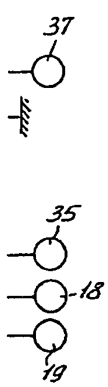
SHEETS 1 & 2

Fig. 3





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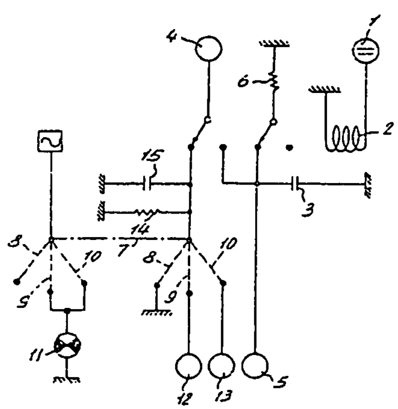


Fig.2

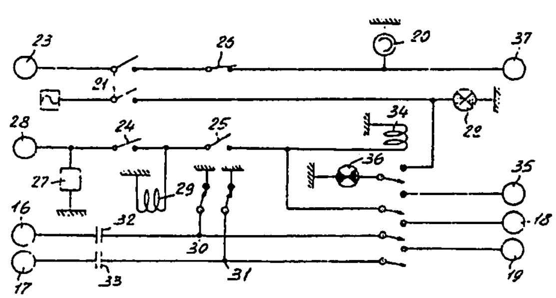


Fig.3

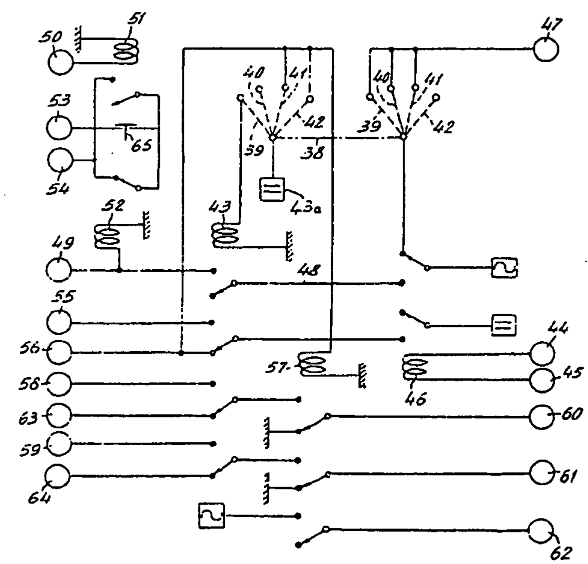
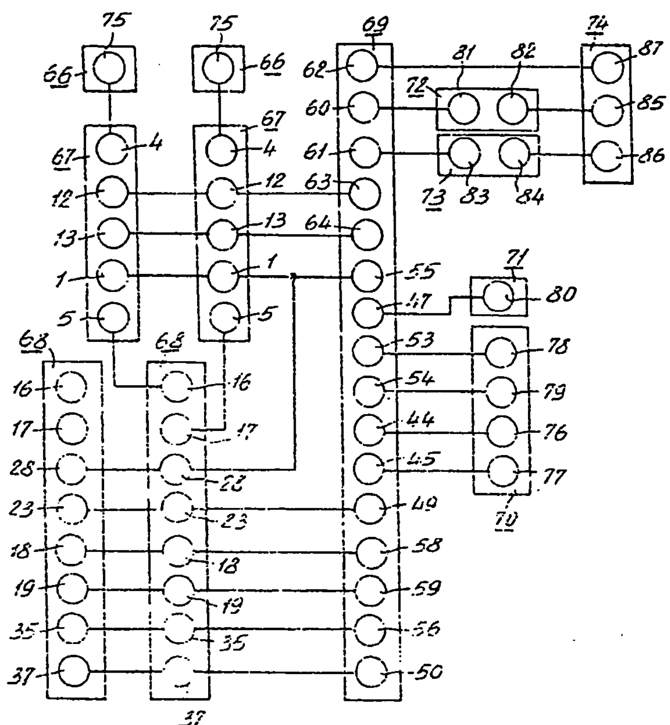


Fig.4



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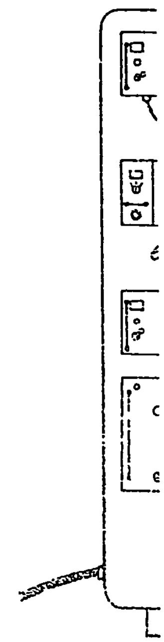

862,212 COMPLETE SPECIFICATION
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SHEETS 3 & 4

Fig. 5

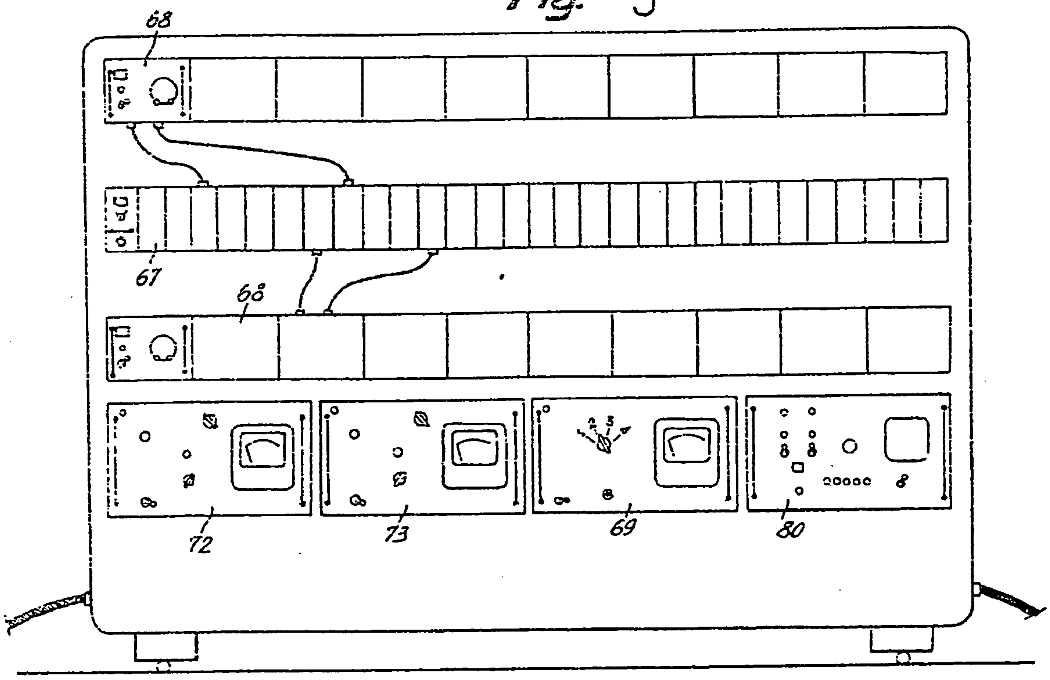

Fig.4

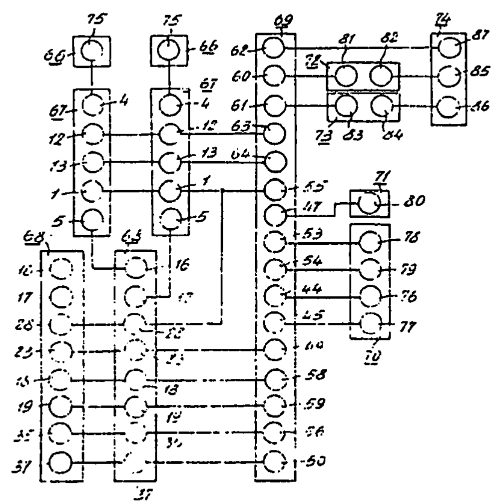

Fig. 5